DQM Standard Operating Procedure (SOP) 3.1.4.1

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Measurement of pH with a Liquid Indicator Kit

(This paragraph is common to all DQM SOPs. If you have seen it already, please skip to Section 1 below). This is a new type of guidance, created as part of the Data Quality Management (DQM) System implemented by the Clean Water Team (CWT) to support collection of reliable data of known quality in a fully documented, scientifically defensible manner.

1.0 About this SOP

These instructions describe how to measure pH using one of several liquid indicator kits available in aquarium stores or from monitoring equipment manufacturers. The kits work by adding a concentrated "reagent", which is a mixture of pH indicators, to the tested sample and comparing the color to a color chart or a plastic color wheel in a comparator. Please refer to DQM-IP-3.1.4(pH), available with the Clean Water Team, for background information on the different ways to measure pH. The Instrument code used for pH liquid indicator kits in this and other DQM materials is "PHLQ".

(This paragraph is common to all Instrument-specific DQM-SOPs). The sections of this SOP are organized as follows: Equipment list, maintenance and storage, accuracy checks, pH measurement, monitoring tips, and detailed guidance on how to control, check, record, and report (CCRR) the accuracy and the precision of the measurements. Contact information for further assistance is provided at the end of this SOP. In must be noted that there are many other SOPs, available from different organizations, which also provide instructions for the use of pH kits. However, the objective of this particular SOP is to provide a new type of guidance as part of the Data Quality Management (DQM) System implemented by the Clean Water Team (CWT) of the State Water Resources Control Board. It provides guidance at the level of detail and specificity that will allow users to generate reliable data of known quality in a fully documented, scientifically defensible manner.

2.0 Equipment List

Apart from this SOP and the pH indicator kit itself, you will need the following:

- Standard pH buffers
- "Distilled water" in a squirt bottle
- Liquid Waste Container (a wide-mouth jar for used reagents and buffers)
- "Field Data Sheet for Water Quality Monitoring" and instructions in SOP-9.2.1.1(Field)
- "Calibration and Accuracy Checks Sheet" and instructions in SOP-9.2.1.2(Calib)

The "distilled water" referred to in the instruction is sold in supermarkets as "distilled water", "deionized water", "purified water", or "drinking water", and these are normally prepared by ion-exchange resins or reverse osmosis. The essential feature is zero conductivity and a lack of contaminants, although there are usually trace levels of nutrients and other chemicals.

3.0 Maintenance and Storage

The liquid indicator pH kits are low-maintenance devices and can be stored anywhere, preferably in a cool place in the dark. Avoid exposure of the reagents or the color charts to direct sunlight.

4.0 Accuracy Checks and Record Keeping

You cannot adjust the output of a liquid pH kit but you can test whether the output is accurate by checking what the kit "reads" in a Standard buffer solution. Make sure you have colorless standards, and test it in the same way you are instructed to test your samples (see below). Use at least two Standard buffers, one of pH 7 and the other at pH 9 or 10. The buffers for pH 4 are available but they are less useful for the range of pH you may encounter in the environment. When you conduct an accuracy check, be sure to use the "DQM Calibration and Accuracy Checks Sheet" provided with its instructions (DQM-SOP-9.2.1.2); this form has placeholders ("Fields") for all the documentation you will need to provide, and is essentially identical to the spreadsheet table in your Excel Project File.

5.0 pH measurements

Step 5.1 Record the Instrument ID which is written on your kit in the appropriate field, in the pH row on the "DQM Field Data Sheet for Water Quality Monitoring"

Step 5.2 Pour some of your water sample into the test tube provided with your kit.

Step 5.3 Add a few drops of reagent (see how many drops you need in your manufacturer's instructions) into the tube, cap, and mix.

Step 5.4 When the color stabilizes, compare the hue to the color chart or the color wheel provided with your kit. Compare the color in the same environment each time. Try to have the same background (white preferred) with the light (white) coming from the same direction.

Step 5.5 Identify the value represented by the color panel that best fits the color of your treated sample, and record it in the Result column in the "DQM Field Data Sheet for Water Quality Monitoring". If you think that the color in the sample is between two panels, e.g., between pH 7 and pH 7.5, write "7.3" in the Result column and "7-7.5" in the Bracket column in the "DQM Field Data Sheet for Water Quality Monitoring". In this case, the number 7.3 will go into the database, and the data users will know that you thought it was more than 7 and less than 7.5 but did not have a panel for the exact value.

Step 5.6 After completing the test and recording the result, pour the treated sample into the liquid waste container and rinse the test tube with DI.

6.0 Monitoring Tips

When you familiarize yourself with a new kit, experiment with doing the color comparison at different light conditions, e.g., in direct sunlight, in the shade, under artificial light source, with the light ahead of you or behind you, etc. You will see differences and develop a sense of what's the best lighting for your kit. Then, be consistent in the way you do the color comparison.

Different people may have different perception of color. It is recommended to have at least two people "read" the output of your pH sample (within the first minute after exposure to air) and to record the second opinion on the same row as the Result, in the "**2nd/dup/rep/dil**" column of the "DQM Field Data Sheet for Water Quality Monitoring" (see SOP-9.2.1.1).

7.0 Accuracy and Precision CCRR (control, check, record, and report)

7.1 Accuracy

Accuracy is the extent of agreement between an observed value (measurement result) and the accepted, or true, value of the parameter being measured. Because you cannot adjust the reading of your PHLQ kit, the only way you can control its

accuracy is to protect it from direct sunlight and other deteriorating factors. However, you can check the accuracy of your kit by testing a Standard Buffer. Follow the instructions in Section 4.0 above and record your activities on the "DQM Calibration and Accuracy Checks Sheet". Some Standard buffer solutions may contain substances that interact with the liquid indicators and create interference; this may result in biased reading (i.e., the wrong color). Ask your technical liaison about different products. To support your accuracy check with other, independent checks, take your kits and Residential Standards to Instrument Calibration events and try different buffers, and also compare your results with the reading of a calibrated pH electrode.

How often should you run accuracy checks? Once every few weeks is usually sufficient. Generally, frequency of accuracy checks will vary depending on the scenario:

- Snapshots and other one-time monitoring events – conduct an accuracy check with two Standard buffers before the event or as soon as you can after the event. Record the reading of your PHLQ kit when added to each of the Standards.
- Routine monitoring – conduct accuracy checks with two buffers every 10 weeks. Record the reading of your PHLQ kit when added to each of the Standards

Standard buffers have a tendency to change over time as well, and it is a good practice to compare your "Resident" Standard with an External Standard from time to time. The potential drift in the Resident Standard is your **second measure of accuracy**. Comparisons with External Standard can be done at regional Intercalibration Exercise events, otherwise known as "instrument calibration party"; it is your responsibility to attend, bring your own Resident Standard and keep records as to how it compares to the External Standard on a copy of the Comparisons of Standard data sheet.

Because the measurement increment (i.e., resolution) of most PHLQ kits is around 0.5 pH units, chances are that drift in the reagents' response, or fading of the color chart, or drift in the Resident Standard will be smaller than the measurement increment. Thus, often the inaccuracy of the kits is contained within the resolution, and will be reported as "less than the resolution" based on your supporting accuracy checks. In fact, if the kit is inaccurate to an extent that is larger than 0.5 pH units, it is recommended to replace the reagents or the entire kit.

7.2 Precision

The precision of your kit is a measure of how close repeated measurements, done with the same kit, are to each other. You can control the precision of your instrument by eliminating sources of error or reducing their effect on the result of the measurements, for example by waiting for the reading to stabilize, using the same illumination conditions every time, and adhering to consistent measurement conditions in terms of sample volume, temperature, mixing, etc.

To check precision, collect two samples from the water body at the same time and measure their pH; these "field duplicates" are a part of your routine Field QA/QC. You can also have two people measure pH of the same sample, or otherwise generate sets of "replicate" results that pertain to the same sample. Record the additional measurement results in the "**2nd/rep/dup/dil"** field on your "DQM Field Data Sheet for Water Quality Monitoring" (see DQM-SOP-9.2.1.1). Generate such pairs every ten weeks and every time you introduce new monitors to your team. As in the case of accuracy, chances are that the error related to low precision falls within the resolution and will be reported as "less than the resolution" based on your supporting precision checks.

7.3 Blanks

Blanks are meaningless in the case of liquid pH indicator kits (and all other pH measurement devices) because the indicators will have their own color even in distilled water. Actually, pH of zero is as acid as it ever gets!

7.4 CCRR Definitions

(This section is common to all Instrument-specific DQM-SOPs) These terms are defined here because they are essential for understanding the instructions. These and many other terms are defined in the Glossary at the end of the generic SOPs for Field Operators (DQM-SOP-9.2.1.1(Field) and DQM-SOP-9.2.1.2(Calib), and in the comprehensive Compendium glossary..

Instrument: a probe, electrode, reagent kit, indicator strip, or any other type of device used for field or laboratory measurements.

Accuracy Check: Comparison of the reading, or output, of a measurement device with a value believed to be the "true" value. The "true" value may be represented by any Standard Material (e.g., known natural reference conditions such as freezing point, Standard Solution, etc). An "Accuracy Check" is different from a Calibration, since it is only a comparison and does not result in an adjustment of the reading of the measurement device.

Calibration (or Calibration Adjustment): Modification of the output of an adjustable-reading instrument, to make it reflect a value that represents the "true

value" (as manifested by a given Standard or by a natural value). Note: The EPA's definition for "Calibration" is, essentially, a combination of "accuracy check (comparison) and adjustment if needed"; it is not specific enough for communication of what you did when you say "I calibrated the instrument".

Standard Material: A catch-all term for Solutions (e.g., Standard Buffer), devices (e.g., Certified thermometer), or natural reference points (e.g., Water saturated with dissolved oxygen at a given temperature), that represent a value believed to be the "true" value.

Standard Solution: A solution containing a known concentration of a substance or has a known property, prepared or purchased for use in the analytical laboratory or in the field. Each bottle of these types of Standards has a **unique Standard ID,** for example "STB-EC2". Every bottle of Standard with its unique ID can be described in one or more of the following definitions:

- "**Resident Standards**" – solutions that each monitoring entity or group owns and uses routinely for calibration and/or accuracy checks.
- "**External Standards**" - solutions used in events such as Intercalibration Exercises, often brought by the QA/QC officer for comparison with the Resident Standards brought by the participating groups;
- "**Certified Standards**" include any Standard that is traceable to NIST or ASTM. Resident and External Standards can all be Certified Standards as well. A Certified Standard is considered the "ultimate authority" if valid, i.e., if the bottle was (a) used before the expiration date; (b) has been stored tightly capped; and (c) has not been exposed to extreme temperatures or sunlight.

8.0 Sources and Resources

(This section is common to all DQM-SOPs, except for the title and SOP number in the citation) This SOP is an integral part of the Data Quality Management (DQM) System implemented by the Clean Water Team, the Citizen Monitoring Program of the California State Water Resources Control Board.

For an electronic copy, to find many more CWT guidance documents, or to find the contact information for your Regional CWT Coordinator, visit our website at www.swrcb.ca.gov/nps/volunteer.html

If you wish to cite this SOP in other texts you can use "CWT 2004" and reference it as follows:
"Clean Water Team (CWT) 2004. Measurement of pH with liquid indicator kits, DQM SOP-3.1.4.1. in: The Clean Water Team Guidance Compendium for Watershed Monitoring and Assessment, Version 2.0. Division of Water Quality, California State Water Resources Control Board (SWRCB), Sacramento, CA."